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Supporting Information

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Enantioselective Assembly of a Ruthenium(II) Polypyridyl Complex into a Double Helix**

Kristof Van Hecke, Thomas Cardinaels, Peter Nockemann, Jeroen Jacobs, Louis Vanpraet, Tatjana N. Parac-Vogt, Rik Van Deun, Koen Binnemans, and Luc Van Meervelt*

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Supporting Information

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Materials and Methods

Luminescence study of an aqueous solution of the $[Ru(bipy)_2(dppzCl_2)]Cl_2$ complex

Ru(II) polypyridine complexes are well known for their luminescence properties, e.g. the Ru tris bipyridyl complex $[Ru(bipy)_3]^{2+}$ serves as a standard for quantum yield measurements.

The luminescence of an aqueous solution of the $[Ru(bipy)_2(dppzCl_2)]Cl_2$ complex (3.75 mg/mL) was studied by recording steady state emission and excitation spectra.

Upon excitation at 465 nm, the solution shows a broad emission band with a maximum at 620 nm (fig. S6). This band can be attributed to a charge transfer transition, typically seen in Ru(II) polypyridine complexes (*29*, *18*).

Monitoring the emission at 620 nm, the excitation wavelength was varied in a range 250-500 nm to record an excitation spectrum (fig. S7). This spectrum shows several bands. The lowest energy (longest wavelength) absorption band at around 450 nm is typically attributed to a metal-to-ligand charge transfer transition (MLCT) $\pi^* \leftarrow d_\pi(Ru)$, whereas the bands at 280 and 330 nm are usually attributed to intraligand $\pi^* \leftarrow \pi$ transitions (*17*). The spiky features on top of the 450 nm band are Xe emission lines, resulting from an incomplete correction for the Xe lamp output, due to different slit widths used to record the Xe lamp output correction file and this excitation spectrum.

References

17. G. Albano, P. Belser, L. De Cola, M. T. Gandolfi, *Chem. Commun.* **1999**, 1171-1172.

18. B. W. Jing, M. H. Zhang, T. Shen, *Spectrochim. Acta, Part A*, **2004**, *60*, 2635-2641.

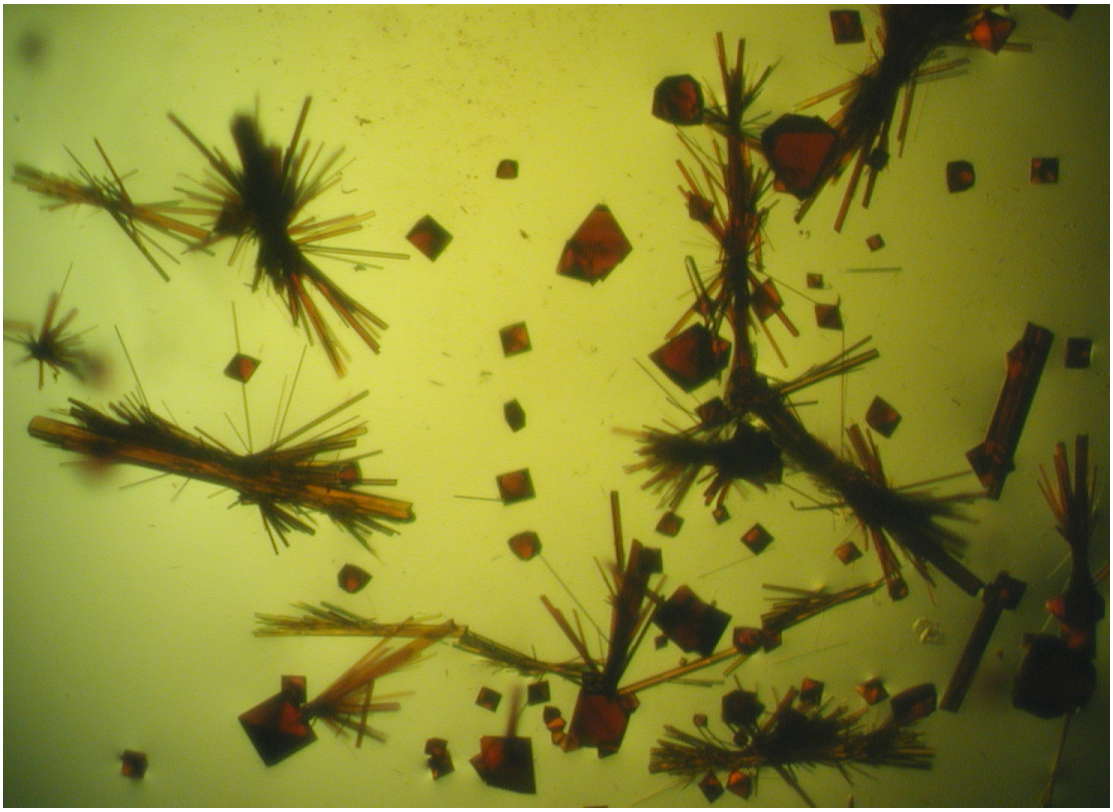

Figure 1. Typical "block" and "rod" shaped crystals of the Λ-$[Ru(bipy)_2(dppzCl_2)]Cl_2$ complex, obtained by the sitting-drop vapor-diffusion method. The largest rod is approximately 0.4 mm in length.

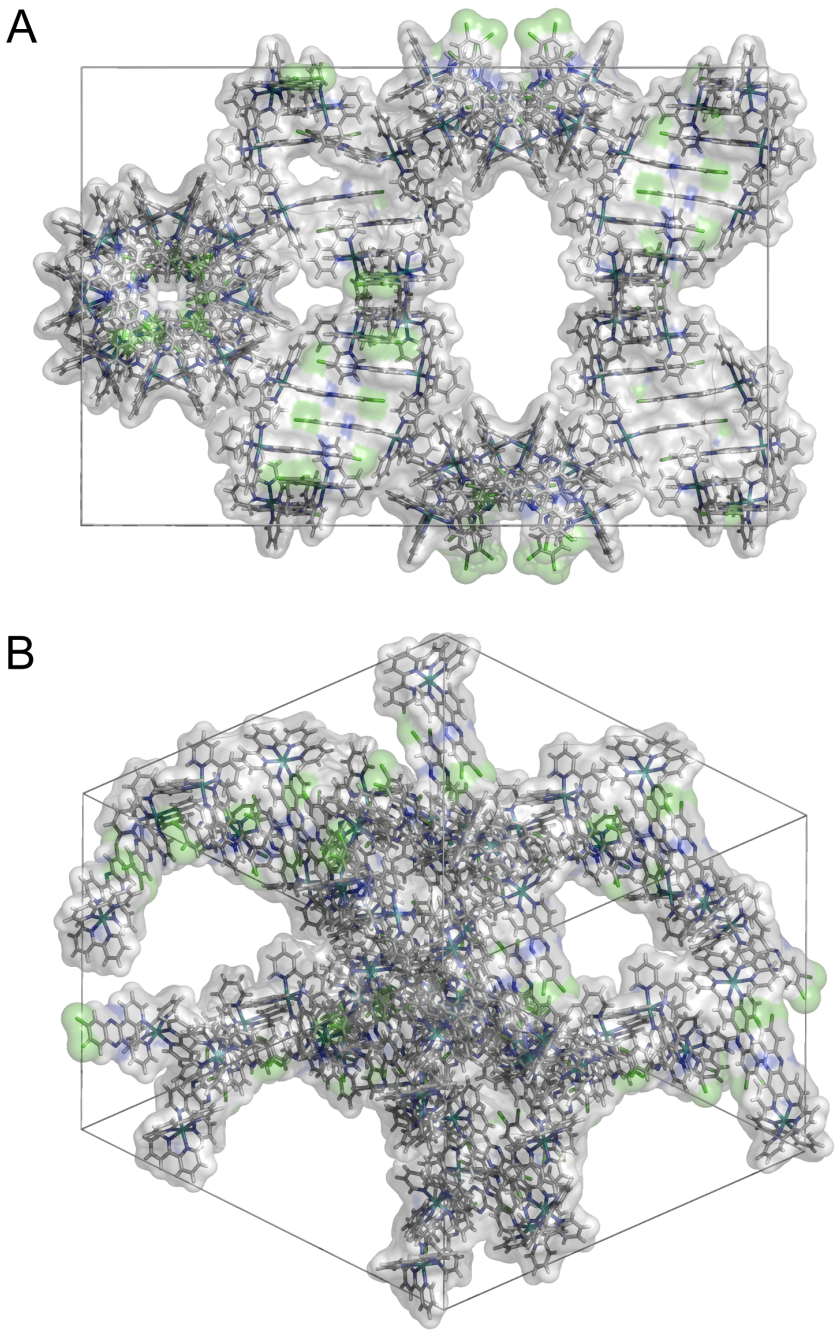

Figure 2. A) For polymorph **1**, a view along the crystallographic *b*-axis illustrates the presence of huge channels (74.9% of the unit cell volume or 150904 Å^3 is void when omitting the water molecules, including water molecules gives 55.8% and 112389 Å^3). B) For polymorph **2**, a view along the [111]-direction illustrates the presence of channels (58.1% of the unit cell volume is void or 70939 Å^3, including the water molecules gives 39.8% and 48577 Å^3).

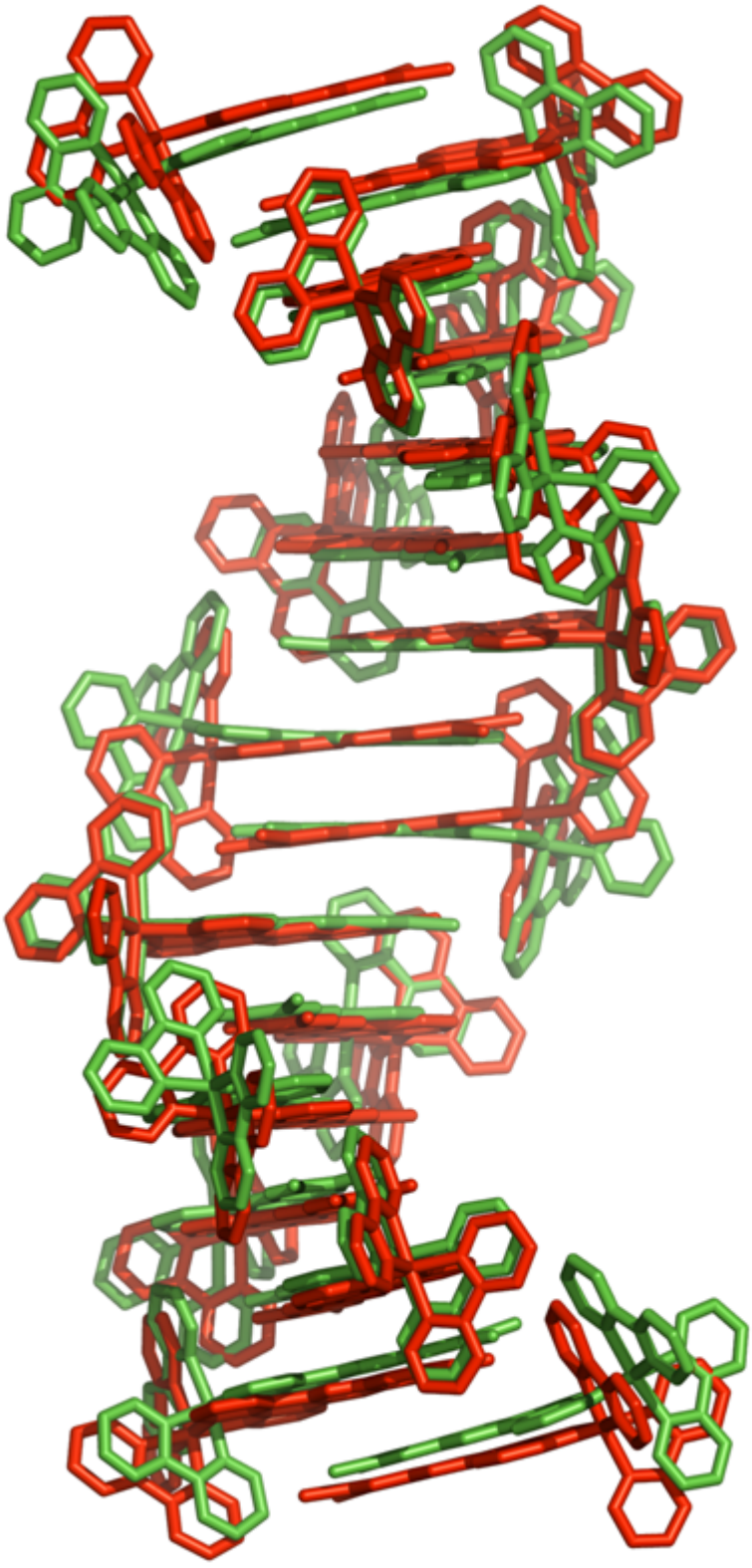

Figure 3. Least-squares fit of the full helical repeats of the structures of polymorph **1** (green) and polymorph **2** (red) (the backbone ruthenium(II) atoms were fitted).

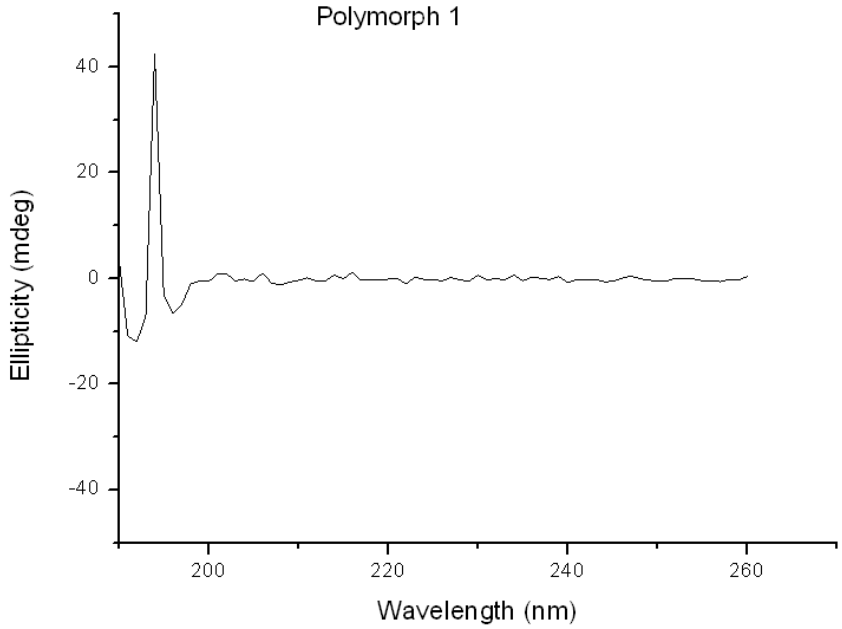

Figure 4. CD spectrum for polymorph **1**. The Ru(II) polypyridyl complex was dissolved in a solution containing 2.0 M sodium chloride and 0.1 M sodium acetate trihydrate, pH 4.6.

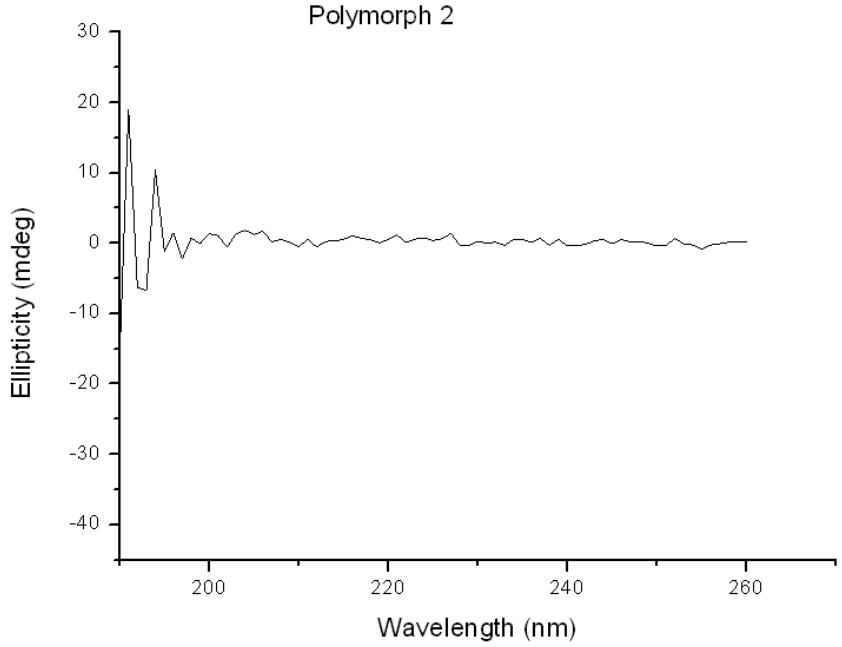

Figure 5. CD spectrum for polymorph **2**. The Ru(II) polypyridyl complex was dissolved in a solution containing 2.0 M sodium chloride and 10% (w/v) PEG 6000.

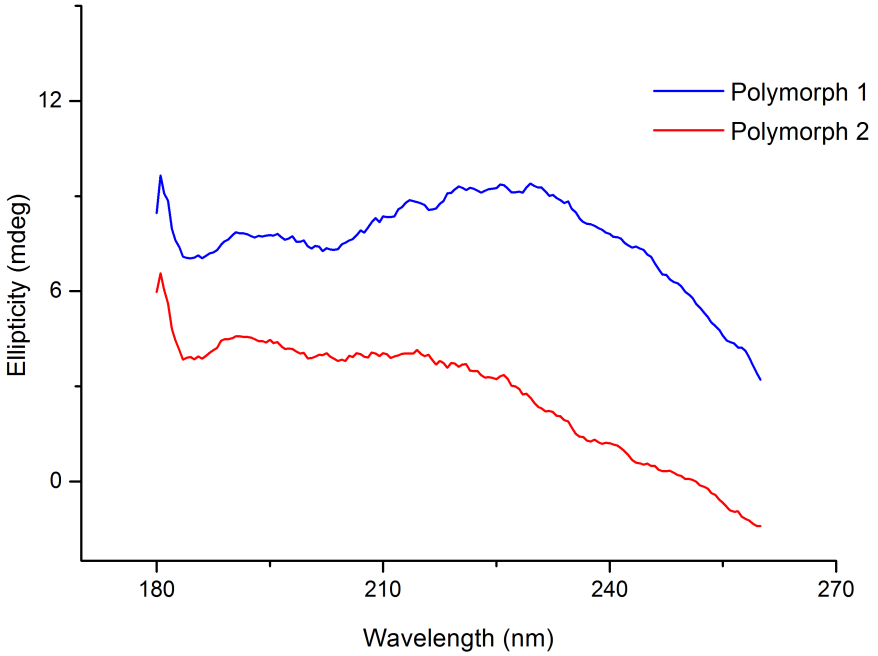

Figure 6. CD spectra for polymorph **1** and polymorph **2**. The obtained crystals of the Λ-Ru(II) polypyridyl complex were isolated and re-dissolved in MQ-water. The weak CD-signals indicate the inefficient racemization of the Λ-enantiomer, which would require Ru(II)-N bond breakage.

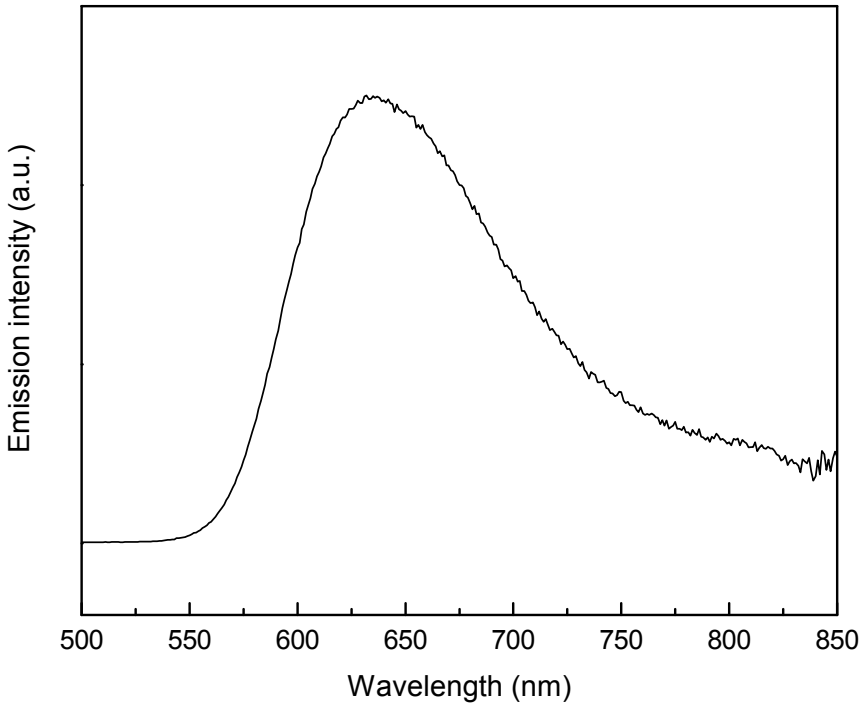

Figure 7. Emission spectrum (excitation wavelength of 465 nm).

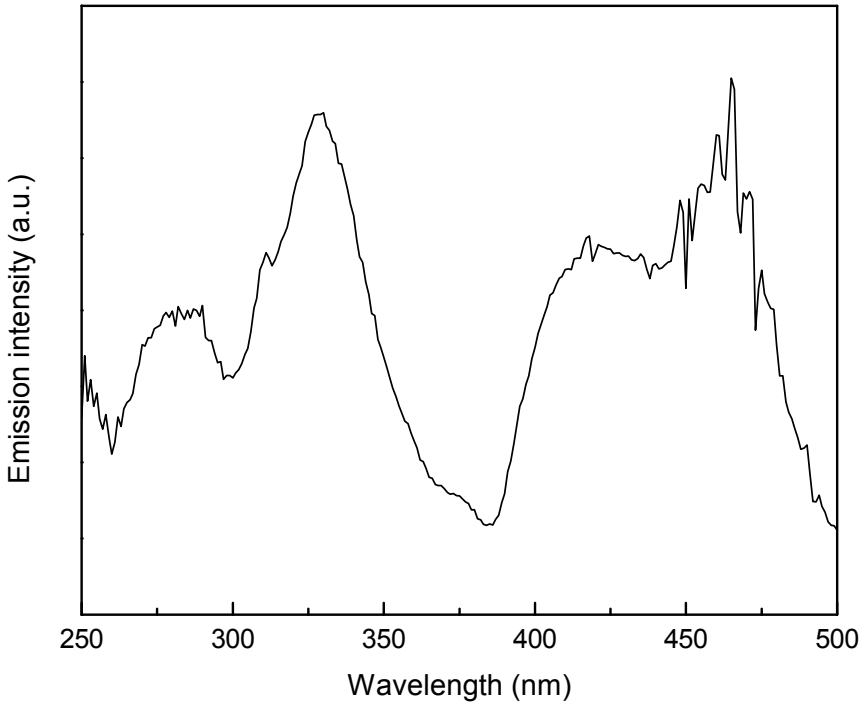

Figure 8. Excitation spectrum (emission wavelength of 620 nm).

Table 1. Data collection and refinement statistics for the structures of polymorphs **1** and **2**. The values between parentheses are for the outermost resolution shell.

	1	**2**
CCDC-number	966366	966367
Space group	$I4_122$ (No. 98)	$C222_1$ (No. 20)
Unit cell parameters (Å)	a = b = 51.210, c = 76.830	a = 53.260, b = 56.410, c = 40.630
Resolution range (Å)	42.61 – 1.20 (1.26 – 1.20)	40.63 – 1.30 (1.37 – 1.30)
R_{merge} (%)	6.0 (52.7)	5.9 (51.2)
Mean I/σ(I)	24.4 (5.2)	16.4 (3.6)
No. of unique reflections	16310 (2333)	15164 (2153)
Multiplicity	15.6 (15.4)	7.2 (7.2)
Completeness (%)	99.7 (100)	98.6 (97.5)
Refinement statistics		
Resolution range (Å)	21.30– 1.20	38.73 – 1.30
R_{work}/R_{free}[a] (%)	12.68/14.53	13.72/16.02
Rmsd from ideal geometry		
Bond lengths (Å)	0.015	0.016
Bond angles (°)	1.004	1.461
No. of chloride ions/waters	7/90	17/98
Average B-factors (Å^2)		
Main residues	18.0	17.2
Chloride ions/waters	23.8/36.5	28.4/30.6

[a] R_{free} is calculated using a random 5.05% and 5.01% of data for **1** and **2**, respectively.

Table 2. Overview of the twist angles[a] in the structure of polymorph **1** and polymorph **2** (negative values are due to the left-handed helix).

Polymorph **1**

Numbers complexes[b]	Twist (°)
1, 3 (= 6, 8)	-50.3
3, 5 (= 4, 6)	-38.9
5, 7 (= 2, 4)	-50.2
7, 9	-39.1
9, 11	-50.3
11, 13	-38.9
13, 15	-50.2
Average	-45.4

Polymorph **2**

Numbers complexes[b]	Twist (°)
1, 3	-43.8
3, 5	-49.2
5, 7	-36.0
7, 9	-50.6
9, 11	-38.4
11, 13	-49.5
13, 15	-39.5
Average	-43.9

[a] Twist angles are calculated by (1) defining the line between the Ru atom and the centroid of the dppz ring (without Cl atoms) and (2) calculating the angle between lines of subsequent repeating units.

[b] The complexes are sequentially numbered from top to bottom of the helix, *i.c.* from 1 to 16.